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Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

This Issue

SYNTHETIC LUBRICANT RESEARCH

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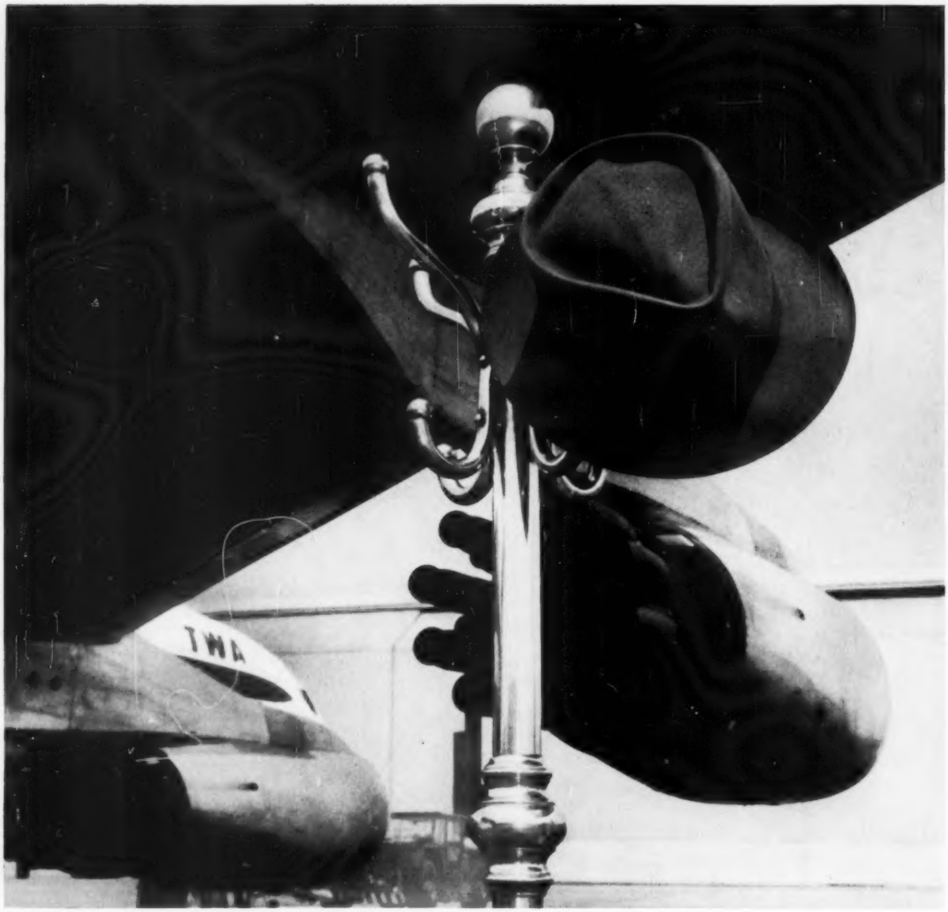

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LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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SYNTHETIC LUBRICANT RESEARCH

SYNTHETIC lubricants have achieved great prominence since the end of World War II primarily because of the rapid development of turbine engine aircraft. Jet aircraft lubrication is in fact the largest single market for synthetic lubricants although other specialized applications consume substantial amounts of these products.

Early jet engine aircraft relied on petroleum products for their lubrication but the low temperature requirements imposed by high altitude flight, coupled with the higher engine operating temperatures could not be met by existing petroleum based oils and greases.

It then became necessary to look for materials combining good low and high temperature properties and as a result synthetic lubricants entered the aircraft picture. Jet aircraft design has advanced greatly since the 1940's and each advance has raised speeds and operating temperatures. As a result lubricant requirements have become more severe and will probably continue to become more so in the future. Development of new and improved lubricants must parallel engineering development so that jet aircraft lubricant research has intensified greatly in the past decade. Synthetic lubricants are also used in instruments, hydraulic systems, heat transfer systems and a variety of other specialty purposes but by and large the progress in synthetic lubricants both fluids and greases has been motivated by the needs of the aircraft industry.

In two previous issues of this publication* the subject of aircraft turbine lubrication was discussed from the standpoint of the engine, its structure and lubricating system and the requirements necessary for its proper lubrication. Some discussion of the classes of lubricants in use and under development was presented, but neither of the previous articles touched on the chemistry of synthetic lubricants. It is the purpose of this issue to present briefly some of the elementary chemistry of synthetic oils and greases and to bring the survey of synthetic lubricants up to date.

The literature published on synthetic lubricants is already enormous and shows no signs of diminishing its present rate of growth. To review even one class of synthetic lubricants in detail would require a sizeable volume. Of necessity this review will touch on high points only.

THE COMPLETE LUBRICANT

The term "lubricant" in the commercial sense has come to mean a mixture of components, the major portion being a fluid (or grease) plus minor amounts of additives. The word "minor" refers only to relative amount of additive present in the mixture and not to a minor role. Indeed, without small amounts of additives most of the synthetic lubricants in use would fall far short of their objectives. The chemistry of additives will not be treated in this issue, however, and the word "lubricant" will refer to the major fluid or grease in question. Additives will be mentioned as the need arises.

*April 1954, March 1959.

Synthetic lubricants are man-made as opposed to naturally-occurring petroleum fluids. Beyond this crude definition there is little that can be said to describe synthetics as a group except that they are mainly organic chemicals.

Certain groups of chemicals have been found to possess the characteristics suitable for lubricating oils and greases. These classes of compounds become important because of one or more outstanding properties, e.g., high viscosity index (small changes in viscosity with changes in temperature) resistance to attack by acids, oxygen, etc. The outstanding properties are usually coupled with one or more undesirable chemical or physical properties, e.g., low stability toward water, high fluid pour point, etc. The research expended on eliminating undesirable properties of a class of lubricants easily equals the effort put into preparing new chemicals for lubrication.

It is difficult to separate lubricants into perfectly distinct classes because of overlapping of one class into another. The separation used in this review is roughly historical, proceeding from the oldest, best known types of synthetic fluids to the newest, experimental ones. Naturally available information becomes scarcer as one progresses to the newest fluids, but enough is known about them to draw at least a rough outline of their possibilities as lubricants.

LIQUID LUBRICANTS

Polyolefins

Of historic importance were the polyolefins first prepared on a large scale in this country in the 1930's and in Germany during World War II. When ethylene or propylene was heated with an acid catalyst under pressure, the process known as polymerization set in which resulted in the formation of long hydrocarbon chains:

$$CH_3{-}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}{-}CH_3$$

As expected these chains or polymers resembled the petroleum oils then in use. Because they represented a reasonably priced petroleum supplement the polyolefins were used extensively by the Germans in World War II. Later researches have shown that olefins can be polymerized with other kinds of catalysts and also without catalysts at higher temperatures and pressures. Unfortunately there are many reaction variables influencing both the yield and the quality of the product in addition to which only certain olefin stocks can be polymerized economically. Olefin polymers are not presently a large factor in the synthetic lubricant field but the experience gained in those researches has provided some fundamental structural guides applicable in many other areas.

Halogenated Hydrocarbons

One method of modifying hydrocarbons to produce lubricating oils which has received much attention is to substitute fluorine or chlorine for hydrogen. Fluorocarbons and chlorofluorocarbons are familiar as refrigerants (Freons). Fluorocarbons are synthesized by heating a hydrocarbon with gaseous hydrogen fluoride or by passing a gaseous hydrocarbon over a heated bed of a metallic fluoride, such as cobalt fluoride. Commercial processes have used kerosine and lubricating oil hydrocarbons as fluorination charge stock and the products have generally been oils of light to medium viscosity. Fluoroolefins are prepared from chlorinated hydrocarbons and hydrogen fluoride and the olefin is then polymerized. Just as with hydrocarbon olefins, the resultant polymers are built up of repeating units. The backbone of the fluorocarbon polymer is a chain of $-{-}{-}CF_2{-}CF_2{-}CF_2{-}CF_2{-}{-}{-}$ units.

Commercially available polymers come in a wide range of liquids and solids. Fluorocarbons are unusual chemicals. They are very resistant to attack by acids, alkali and oxidizing agents. They will not decompose even when heated to about 800°F. Unfortunately, the pour points and viscosity index of these molecules are very poor, their boiling points are much lower than corresponding hydrocarbons and they are insoluble in most organic solvents and lubricants. Fluorocarbons will not dissolve many of the chemicals used as lubricant additives.

The introduction of chlorine into a fluorocarbon moderates its properties somewhat. Boiling points are higher and solubility improves. The viscosity indices of chlorofluorocarbons are somewhat better than the fluorocarbons but are still below zero, their resistance to chemical attack is not greatly different from fluorocarbons. The obvious desirability of great thermal stability and chemical inertness in a lubricant has led chemists to synthesize a large number of "halocarbons" in an effort to improve their physical properties and thus extend their use but these attempts have generally been unsuccessful. Excessive cost has also prevented the wide acceptance of fluorolubes but they are used in specialty jobs such as lubricating metals in strongly oxidizing atmospheres like those of fluorine or chlorine vapors.

Fluorination techniques have been extended to other classes of potential lubricants e.g. esters in the hope that fluorine would impart the same chemical resistivity to the ester. This goal has been achieved to an extent and the subject will be treated in a later section.

Halogenation of aromatics is a well known procedure:

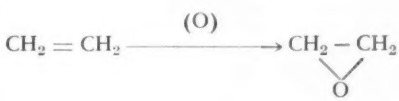
Aromatic hydrocarbon + chlorine $\longrightarrow$
Chlorinated aromatic.

Chlorinated aromatics are widely known for their heat transfer properties, flame resistance and boundary lubrication activity. These compounds (chlorinated bi- and polyphenyls) suffer the same physical drawbacks as other halocarbons, namely poor viscosity-temperature properties and high freezing points, but again they possess excellent thermal and oxidative stability easily surpassing their parent aromatic hydrocarbons. The chloroaromatics are used also as specialty lubricants and hydraulic fluids.

Polyalkylene Glycols

Polymers of ethylene-, propylene-, and higher alkyl ethers, developed commercially more than a decade ago, are called the polyalkylene glycol lubricants. The raw materials for their synthesis are the same petroleum-derived olefins used in polyolefin lubricants. In this case the olefin is first oxidized by any one of a wide variety of processes to the cyclic ether:

alkylene ether



The alkylene ether is then polymerized to the desired chain length by treatment with a base catalyst:

$$\text{------ } O\text{–}CH_2\text{–}CH_2 \left[- O\text{–}CH_2\text{–}CH_2 \right]$$
$$\text{–}O\text{–}CH_2\text{–}CH_2\text{–}O \text{ ------}$$

Here again there is a repeating unit (in brackets) which serves as the building block of the polymer. In pure alkylene oxide polymers the chains end in hydroxyl groups –OH, which are present also in alcohols, R–OH and water, H–OH. By adding an alcohol or phenol to the oxide being polymerized, mono or diethers can be formed. Mixed alkylene oxides (such as ethylene and propylene oxides) will co-polymerize, yielding complex mixed polymers.

Depending upon the choice of starting materials and the control of reaction variables, the physical characteristics of the polymers may be varied between wide limits. The high percentage of oxygen and the presence of OH groups in the polyglycols gives rise to good viscosity-temperature slopes; i.e., viscosity indices of 130 to 180; pour points are often –40° to –65°F and lubricity and anti-wear properties are excellent. This favorable combination of physical properties has led to wide industrial use of polyglycol lubricants in a variety of applications (hydraulic fluids, heat-transfer media, glass manufacturing machinery). The polyalkylene oxide chain is subject to thermal and oxidative attack at temperatures at which jet aircraft presently operate; thus polyalkylene glycol fluids themselves are unsuitable for such high temperature operation. However polyalkylene glycols have been used as starting materials in the preparation of synthetic ester jet lubricants which are discussed in the following section.

Esters

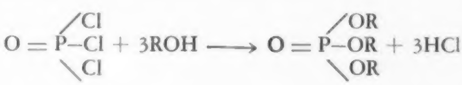
By far the largest class of compounds favored as synthetic lubricants are the esters. This class includes compounds not only of carbon but also of phosphorus and silicon.

Phosphorus compounds are treated first, organic esters next and silicates are combined with other silicon compounds in a later section.

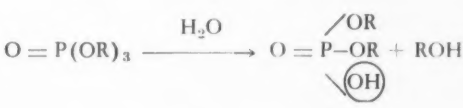
Phosphate Esters

Phosphate esters are derived from phosphoric acid by reaction with alcohols or phenols.

Phosphates can be prepared by treating phosphorous oxytrichloride with an alcohol:



but recently it has become feasible to prepare aromatic phosphates from phosphoric acid and phenols by a special technique which reduces the water formed to a very low level (less than 0.1%). Alkyl phosphates are fluid to low temperatures (–70°F), their viscosity indices range from minus 100 to plus 150 and high molecular weight members have low volatility. Two properties which have resulted in the wide application of phosphates are their non-flammability and their lubricity. The low flammability has been a boon in protecting hydraulic systems and the so-called "extreme pressure" activity of certain phosphates has led to their inclusion in many lubricant formulations as additives. As is the case with all esters, however, phosphates are attacked by water and they begin to revert to an acid form (the encircled OH group in the following equation) which is very corrosive to metals.



This hydrolysis reaction takes place more rapidly with increases in temperature and moisture and may render a fluid useless in a matter of days.

Much of the research in phosphate esters has gone into modifying the various OR groups attached to phosphorous to improve resistance to hydrolysis. The more recent products have been aromatic phosphates derived from substituted phenols and similar aromatic types.

Phosphates are attacked more readily by oxygen than by simple heating in absence of air so that a non-oxidizing atmosphere such as a hydraulic system is suitable for their best application.

One of the largest applications of phosphate esters has been in the field of fire resistant hydraulic fluids. Because of the high fire points (above 600°F) and autoignition points (above 1000°F) of some phosphates, these esters have long been considered safety hydraulic fluids for such applications as furnace, welding, and glassmaking machinery, aircraft and many other operations.

Organic Acid Esters

Organic acid esters represent the most important group of commercial synthetic lubricants in use.

Ester based fluids currently perform in both military and commercial jet aircraft and indications are that they will continue to do so for some years to come. The esters have no single outstanding property, but they have a combination of good physical and chemical properties which suffice for present jet lubricant requirements.

Esterification is one of the oldest, most thoroughly studied reactions of organic chemistry. The reaction itself is a simple one generally involving an organic acid and an alcohol.

$$\text{acid} + \text{alcohol} \underset{\text{solvent}}{\overset{\text{catalyst}}{\rightleftarrows}} \text{ester} + \text{water}$$

Because esters react with water, the water formed in the reaction is removed generally by distillation. Yields from this reaction are high (90-100%) and the mechanics are simple, both of which are economically favorable. Diesters which are products of dibasic acid with alcohols (or glycols with monobasic acids) constitute the most commercially important group of synthetic lubricants.

The group of diesters derived from adipic (C_6), azelaic (C_9) or sebacic (C_{10}) dibasic acids and C_8–C_9 alcohols have desirably high boiling points, are fluid to below −75°F, have excellent viscosity indices of 150-160, and are good solvents for organic compounds. This solvent power is fortunate for in certain applications it is necessary to inhibit the ester against oxidation, metal corrosion and excessive foaming and also to improve its lubricating quality. These are the functions performed by the additives which must be blended with the ester. Such diester blends are qualified against military specification MIL-L-7808* and are used in many military applications as well as commercial jet airplanes. One property of esters which does not respond to improvement by additives is thermal stability. Esters begin to break down at temperatures of about 550°F yielding olefins and acids. This reaction can be measured on a sensitive pressure device and a plot of this measurement is given in Figure 1. A recent advance in ester technology has been the discovery that by proper choice of starting materials this type of thermal breakdown can be avoided and the useful temperature range of esters can be extended as much as 50°F.

Since esterification is essentially a reaction between acid and alcohol groups it is possible to cause esterification with molecules containing more than one of these groups. By combining a dibasic acid and a glycol it is possible to form a high molecular weight polymer called a polyester.

High molecular weight polyesters are generally quite viscous and are not used in lubricants but the size of these polymers can be moderated by the addition of a monoalcohol or acid.

Such esters are called "complex esters". The name is suitable because complex esters are not pure chemicals but mixtures of diesters and polyesters of various molecular weights. Complex esters are more viscous than diesters and are often blended with diesters to achieve a higher viscosity while maintaining good low temperature properties.

Recalling the chemical inertness of fluorocarbons it was not unusual that research efforts were made to combine the fluorocarbon chain with the ester group. Such fluoroesters do indeed possess enhanced thermal and oxidative stability but the rigid structure formed by the fluorocarbon chains raises pour points and volatilities to the point where the fluoroesters are not considered usable for the broad temperature range originally intended. This is yet another case of improvement going hand in hand with detriment. Structural modification of esters continues to be an active area of research.

Silicon Compounds

The main reason for the application of silicon compounds to lubrication becomes clear when one considers their incomparable viscosity-temperature properties. Table I indicates that as a group, these compounds have the least change of viscosity with temperature of any class of lubricants.

With this outstanding quality as a basis, thousands of compounds have been prepared hoping to remedy one or another of the inevitable deficiencies which characterize silicon derivatives as well as other types of synthetic fluids.

Alkyl and Aromatic Silanes

Silicon compounds of particular interest in lub-

* For the complete descriptive number of this and other specifications mentioned in this article please refer to Tables II and III.

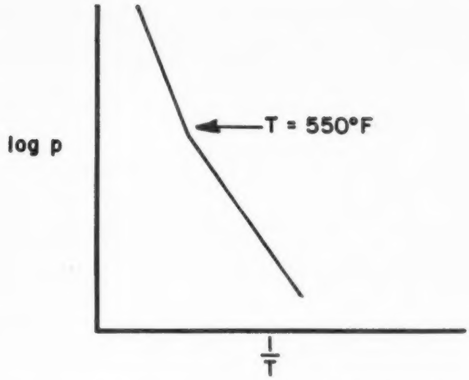
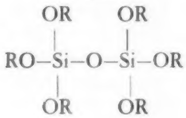


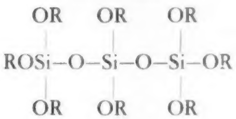
Figure 1 — Plot of vapor pressure versus reciprocal of temperature for Di-2-ethyl hexyl sebacate. Change of slope indicates initial thermal breakdown. Patterned after Wright Air Development Command Technical Report 53-293.

ricants are the alkyl and aromatic silanes, SiR_4, the silicates $Si(OR)_4$ and polymers of the silicates, the di- and trisiloxanes and silicones:

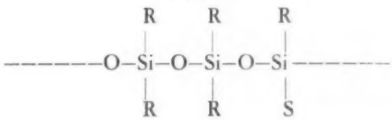
disiloxane



trisiloxane



silicone



Silanes are generally made by treating silicon tetrachloride or tetraethylsilicate with an organometallic compound:

Silicon tetrachloride + organometallic ⟶ organosilane

These methods are expensive and not easily adaptable to large scale production. Some simpler, less expensive methods starting with silicon or silica are available and others are under investigation but these reactions generally yield only partial alkylation of silicon. Silanes are very resistant to attack by water, heat and oxygen. A group of silanes has been prepared which decomposes less than 10% after exposure to temperatures of 700°F for 8 hours. Their flash points often exceed 550°F and they degrade only slightly in a catalytic oxidation test at 500°F. Invariably this group of fluids have poor low temperature properties. Conversely, a second group of silanes have been made with pour points of −80°F but flash points fall to 400°F and high temperature properties are correspondingly poorer. Compromises are widely sought after and indications are that they will be found. Some cyclic silanes recently synthesized have pour points below −60°F and boiling points greater than 600°F.

Siloxanes

The esters of silicon are a great deal easier to produce than the silanes. Usually, silicon tetrachloride is treated with an alcohol (or a series of alcohols) to produce the silicate or siloxane:

Silicon tetrachloride + alcohol ⟶ Silicate ester

Disiloxanes and trisiloxanes are prepared from partially chlorinated silicates and water.

Two major difficulties have beset silicate fluids; their instability toward water and their apparent inability to lubricate steel on steel under certain conditions. Both of these problems have received attention but the hydrolytic instability problem has responded somewhat better to structural modifications. By mixing the structure of a silane with a siloxane, greatly improved water resistance has been achieved; such molecules retain their excellent viscosity temperature properties. One such compound is reported as having a viscosity of 7.7 c.s. at 210°F and about 2000 c.s. at −65°F. Heat stability of siloxanes is good at 600°F for periods of 8 hours and oxidation stability is also good. Improvement of hydrolytic stability can be the key to success of these fluids.

Silicon polymers from dimethyl and diphenyl dichlorosilanes have been marketed for some years and high molecular weight species of these are used as foam inhibitors and for viscosity thickening in

TABLE I
Viscosities of a Siloxane, an Ester and a Mineral Oil

Lubricant	Kinematic Viscosity (centistokes) −65°F	210°F
Siloxane	1500	4
Trimethylol propane trioctanoate	15-16000	4
Dewaxed mineral oil	390,000 (extrapolated) (Pour Pt. = −60°F)	4

silicate systems but they have not been accepted as high temperature lubricants for the same reasons previously described for the lower members of the series.

Polyphenyl Ethers

One final class of compounds receiving rigorous attention because of their outstanding potential as high temperature lubricants are the polyphenyl ethers. A typical member of this series,

boils in the same range as a suitable ester, has a flash point above 550°F, a spontaneous ignition temperature of above 1000°F, does not cause appreciable coking deposits even at 800-900°F and begins to break down thermally only at about 850°F. This material will survive catalytic oxidation tests at 600°F for long periods, and it represents a possible prototype for nuclear powered aircraft because of its resistance to degradation at low levels of radiation. Its drawback is that it solidifies at about 200°F. Some modifications of the original structure succeed in lowering the solidification point to about 15°F but even this temperature does not compare with the low temperature range spanned by esters or silicones.

Synthetic procedures for polyphenyl ethers are not attractive since they involve expensive intermediate steps and low overall yields. Much improvement in this area is needed before contemplating million-pound quantities of phenyl ethers for production.

Newer Experimental Base Fluids

Experiments are under way looking into the possibility of using as lubricants liquid metal combinations such as sodium-potassium alloys, high molecular weight inorganic polymers of boron, phosphorous and nitrogen, solid lubricants (molybdenum salts and other inorganic compounds) and organic vapors containing various additives. Little is published in this area and in most cases the applications are quite specific but engineering research may actually open the way for any of these newer types to become functional.

Products From Synthetic Base Fluids

Some of the uses of the various classes of synthetics have been mentioned throughout this discussion. This section will address itself exclusively to esters and their application in aircraft lubrication.

As previously indicated, the March, 1959 issue of this publication covered the subject of synthetic lubricants as applied to turbine engine aircraft in great detail. The reader is referred to that article for a full treatment of the subject. It is pertinent to this discussion, however, to show how the previously-described synthetic esters fit into the requirements of the modern jet aircraft.

There are five main specifications covering the use of liquid synthetics in aircraft turbines and accessory equipment. These five specifications may be grouped according to their viscosity requirements as given in Table II.

The three specifications in Group I have essentially the same requirements except that MIL-L-25336 requires a greater gear-loading capacity than MIL-L-7808, while MIL-C-8188 includes a requirement for rust protection where the others do not. All these specifications include a large array of tests such as oxidation-corrosion, foaming, coking, thermal stability, etc. The synthetics which most satisfactorily meet all the specification tests are the diesters, typified by di-2-ethylhexyl sebacate. The products formulated from the diesters generally include an oxidation inhibitor and a so-called "E.P. additive" to raise the load-carrying property of the ester. In the case of the MIL-L-25336 oil, the gear-loading requirement often necessitates the use of additional E.P. additive (or addi-

TABLE II
Viscosity Limits of Various Specifications

		Kinematic Viscosity Limits at			
Group	Specification	−65°F.	−40°F.	+210°F.	+400°F.
I	MIL-L-7808C, Amend 1	13,000 max		3.0 min	
	MIL-L-25336 (ASG)	"		"	
	MIL-C-8188B, Amend. 1	"		"	
II	D. Eng. RD 2487 (British)		13,000 max	7.5 min	
	Allison EMS-35-F		"	"	
III	MIL-L-9236 (ASG)				3.0 min

tives) to pass the specification limit. The MIL-C-8188 oil will have, in addition to its basic additives, a chemical designed to give added rust protection for engines which may be stored for extended periods of time. The diester oils, first developed for military purposes, are presently being used in commercial aircraft powered by American and some British turbojet engines.

Group II oils are used in American and British turboprop engines (and also in British turbojet engines). The turboprop engine is one in which the jet engine is harnessed to a propeller through a complex system of gears. The general requirements for the lubrication of this engine are similar to those of Group I except for the heavy requirements imposed by the reduction gears. In order to lubricate these gears properly the engine designers specify an oil somewhat more viscous than MIL-L-7808, and some designers include a shear stability requirement.

This problem was solved by blending diesters with high polymers or complex esters to achieve the necessary high and low temperature viscosities, while maintaining good thermal and oxidative stability and necessary gear load carrying ability.

The lone member of Group III, the MIL-L-9236 specification is a changing "target" specification for an oil to be used in an advanced engine operating at higher temperatures and at very high speeds and altitudes. Present diesters deteriorate at these temperatures and more stable materials are required. Thermally stable esters (derivatives of trimethylol propane) have been developed for this purpose but insufficient data are available to evaluate extended performance at high altitudes and temperatures. At present, available ester-based fluids are doing an adequate job in jet airplane lubrication but future prototypes may include design changes which will require materials which are presently in the experimental stages of development.

GREASES

Theoretically any of the several types of synthetic fluids discussed in Section I could be used in compounding greases. In practice only the diesters, polyesters, complex esters and silicone fluids have been used extensively for this purpose because they best provide the combination of properties required in the finished greases. Each of the other types of synthetic lubricants have serious deficiencies which preclude their use. As examples, the polyolefins, halo-olefins and polyphenyl ethers do not possess the necessary low temperature characteristics, the

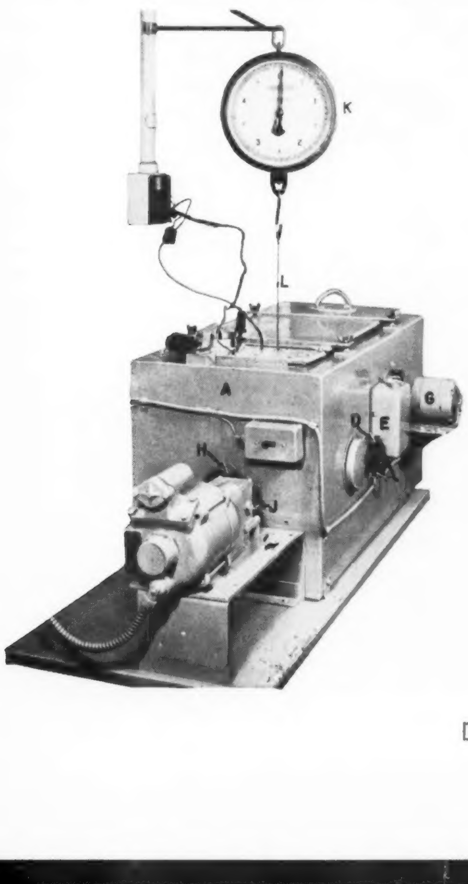


Figure 2 — Test apparatus for measuring bearing starting and running torques at extremely low temperatures.

A. Insulated cold box in which the desired test temperature is obtained and maintained by air circulated through a dry ice compartment by means of an internal fan and its thermostatically controlled motor G.
D. DeKhotinsky thermo-regulator.
E. Mercoid motor switch.
G. Fan motor.
H. Shaft on which the inner race of the test bearing is mounted. (The shaft extends into the cold box and is supported by two ball bearings in its inner and outer walls.)
J. A 900 to 1 ratio speed reducer which drives shaft H at 2 RPM.
K. Test bearing torque scale, spring type, 8" face, 0 to 5 lbs. range.
L. Nylon cord connecting torque scale with outer diameter of test bearing housing.
M. (Illustration below.) Test bearing housing assembly with #204 size test bearing and its inner and outer race clamps.

TABLE III

SUMMARY OF AIRCRAFT SYNTHETIC OIL GREASE SPECIFICATIONS

Designation	MIL-G-7118A	MIL-G-3278A	MIL-G-21164A (ASG)	MIL-G-7421A	MIL-G-25760 (USAF) Amend. 3	MIL-G-25013C
Date of Issue	9-5-58	4-23-56	4-2-59	4-16-54	2-13-59	4-14-59
	Gear, Actuator Screw, For Low and High Temperatures	Aircraft and Instrument, Low & High Temperature	Molybdenum Disulfide, Low and High Temperature	Extreme Low Temperature	Ball and Roller Bearing-Wide Temperature Range	Ball and Roller Bearing-Extreme High Temperature
Dropping Point, °F, min.	325	325	325	325	500	450
Penetration - Unworked, min.	200				200	
- Worked	270-310	260-310	260-310	260-330	260-320	260-330
Worked Stability, 100,000 Strokes, max.	375	375	375	375		375
Bomb Oxidation	210°F	210°F	210°F	210°F	210°F	250°F
psi drop 100 hr. max.	5	5	5	5	5	5
psi drop 500 hr. max.	15	15	25	-	-	-
Water Resistance, % Loss, max.	20	20	20	20	50	5.0
Evaporation 22 hr, % max. (°F)	2.5 (250°)	2.5 (250°)	3.0 (250°)	2.0 (250°)	7.0 (350°)	4.0 (400°)
Oil Separation, 30 hr, % max. (°F)	5.0 (212°)	5.0 (212°)	5.0 (212°)	5.0 (212°)	5.0 (350°)	7.5 (450°)
High Temp Performance, hr. min., (°F)	1000 (250°)	1000 (250°)	1000 (250°)	650 (250°)	400 (350°)	500 (450°)
Mean Hertz Load, kg, min.	30	-	50	-	-	-
Apparent Viscosity	-65°F	-65°F	-65°F	-100°F	-40°F	-65°F
20^{-1} seconds, poises, max.	10,000	10,000	10,000	15,000	15,000	10,000
50^{-1} seconds, poises, max.	6,000	6,000	6,000	-	-	6,000
Low Temperature Torque	-65°F	-65°F	-65°F	-100°F		-65°F
Starting, g-cm/°F, max.	5,000	5,000	5,000	Sec/Rev, 2000		5,000
Running, g-cm/°F, max.	500	500	500	g-cm, 5 max.		500
Bearing Protection Test Rust spots/bearing, max.	3 Small	3 Small	3 Small	-	-	3 Small
Gear Wear, Brass on Steel						
5 lb load, loss mg/1000 cycles, max.	2.5	2.5	-	2.5	-	-
10 lb load, loss mg/1000 cycles, max.	3.5	3.5	-	3.5	-	-
Steel on Steel Wear (Four Ball) Scar Diameter mm, max.	-	-	-	-	1.3	
Dirt Count						Not applicable
25-75 micron, max.	1500	5000	-	7500	5000	
75-125 micron, max.	None	1000	-	1600	1000	
Above 125 micron, max.	None	None	-	None	None	
Copper Corrosion, hr/°F	20/210°	20/210°	24/212°	24/212°	24/212°	24/212°
Bomb, psi, drop, max.	1.0	1.0	-	-	-	-
Oven	-	-	Pass	Pass	Pass	Pass
Storage Stability - 6 months at 100°F						
Penetration - Unworked, min.	200	-	-	-	200	
Penetration - Worked, Points change, max.	±30	±30	±30	±30	-	±30
Range	-	-	-	-	260-320	-
Molybdenum Disulfide, %	-	-	4.5-5.5	-	-	-

polyalkylene glycols lack thermal and oxidation stability and the phosphorous esters are too susceptible to water and to oxidation.

Several materials of the diester, polyester and complex ester types are characterized by excellent viscosity-temperature properties, low volatility, good oxidation resistance and good thermal stability. They also exhibit good additive response and can be thickened to a grease consistency with many of the soap and non-soap thickeners available to the industry. The highly polar nature of the esters imparts excellent lubricity to the greases. The principal limitation of the ester type fluid is a narrower temperature range of application than is required to meet present needs. These materials which can be used at temperatures of the order of −65° or −100°F are limited to a top temperature of 250°F. Conversely materials specifically selected for use at 350° or 400°F usually are not suitable below −40°F.

The silicone type fluids and the greases prepared from them have the best viscosity-temperature properties of any of the commercially available synthetic lubricants. Thermal stability is excellent and volatility is low. They possess a wider temperature range of application than the other type fluids including the ester type materials. A major deficiency of the silicone type products however is their poor lubricity. This deficiency along with their high cost restricts the silicone greases to antifriction bearing applications which do not involve heavy loads or ultra high speeds.

Synthetic Grease Specifications

Synthetic oil greases were first used extensively during World War II. The lubrication of aircraft accessories required a product having a wider operating temperature range than that of conventional mineral oil greases. Military Specification AN-G-3a covered one product for application at temperatures

as low as −67°F, for continuous operation at +250°F and for extended periods at +300°F. The AN-G-3a grease proved to be an outstanding and versatile product. The present version known as MIL-G-3278A Grease is still one of the more widely used of the synthetic oil greases.

The rapid advances in aircraft in recent years have imposed lubrication problems which could not be handled by synthetic oil greases used during the 1940's. Increased speeds and higher altitudes have broadened the operating temperatures from the −67° to +250°F range to the −100° to +450°F range. It is not unusual for equipment to be subjected to these extremes of temperature over relatively short intervals. The emphasis on reducing weight to permit increased pay loads has resulted in a reduction in the size of aircraft accessories and in the clearance between machined parts. This has increased operating temperatures and loads, and reduced the amount of lubricant that can be applied.

Figure 2 illustrates and describes an apparatus that is regularly used to determine the starting and running torques of grease lubricated bearings at low temperatures.

Figure 3 presents four identical high temperature grease test units, the design of which is being considered for standardization by the Coordinating Research Council.

To keep pace with these changes lubricant specifications have been revised and new ones issued. At the present time there are eight Military Specifications covering synthetic oil greases. Most of these cover aircraft applications. Several of these products are finding extensive use in other fields because of their outstanding combination of properties. The requirements of the six more important Military Specification synthetic oil greases are summarized in Table III.

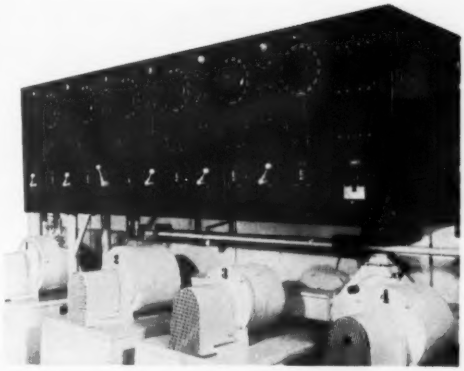


Figure 3 — Battery of four high temperature grease test units.

MIL-G-3278A

This specification provides for the lubrication of aircraft accessories operating in the −65° to +300°F temperature range. It is the most recent modification of the original AN-G-3a grease and incorporates such improvements as a less volatile oil component and rust protection. Specification MIL-G-3278A is expected to be superseded by the MIL-G-7118A specification in the near future which requires improved load carrying capacity and better storage stability but is comparable to MIL-G-3278A in other respects.

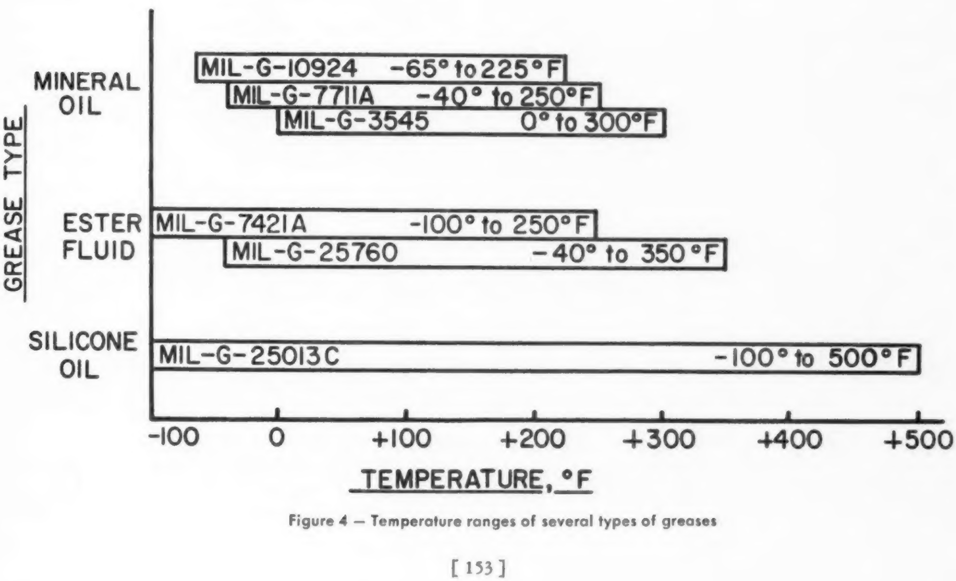
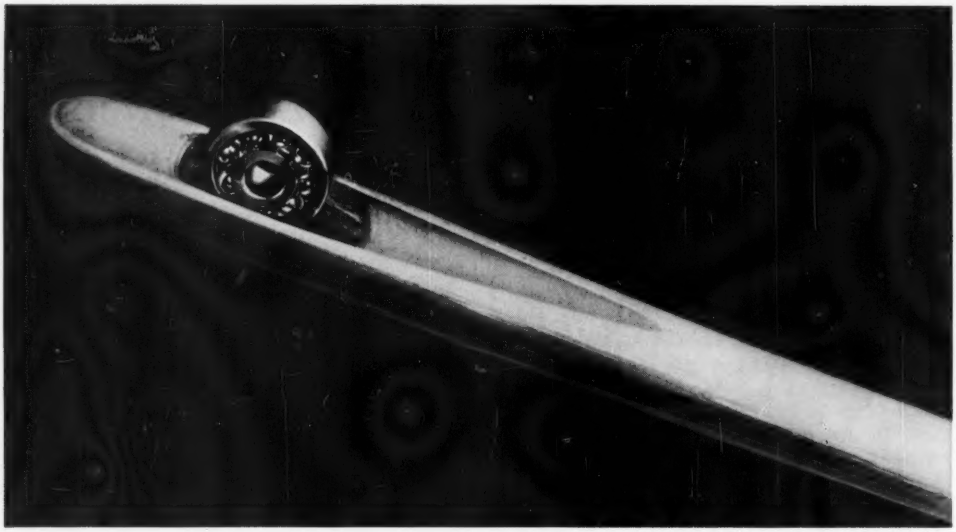


Figure 4 — Temperature ranges of several types of greases



Courtesy of Miniature Precision Bearings Inc.

Figure 5 — A highly magnified picture of a tiny instrument bearing resting in the eye of an ordinary sewing needle. Working under a magnifier the manufacturer usually lubricates such bearings with a tiny drop of grease from the tip of a hypodermic needle.

MIL-G-21164A

This specification covers a MIL-G-7118A grease containing five per cent molybdenum disulfide to further enhance its load carrying capacity, and applies to the lubrication of heavily loaded steel-on-steel surfaces of the plain or sleeve bearing type. The specification states that it is not intended as an antifriction bearing lubricant without prior evaluation. High temperature performance tests involving 204 size ball bearings at 250°F indicate no reduction in performance life over that of the MIL-G-7118A Grease due to the presence of the molybdenum disulfide.

MIL-G-7421A

A product meeting this specification is similar to the MIL-G-3278A type product in many respects. It requires a somewhat lighter synthetic oil to permit the operation of low-torque equipment at temperatures as low as −100°F. High temperature applications are restricted to +225°F for continuous operation and to +250°F for intermittent but extended periods.

MIL-G-25760

This specification covers a wide temperature range grease for use in antifriction bearings operating in the −65° to +350°F range. It is specifically intended as a wheel bearing grease for high speed aircraft. However, it is expected to find much wider application since it combines a number of outstanding properties including operation over a wide temperature range, water resistance, oxidation stability, rust protection and a dropping point above 500°F.

MIL-G-25013C

This specification is intended to apply to ball and roller bearings operating in the temperature range of −65° to +450°F and for continuous operation at the upper limit when the DN Value (bore diameter in mm x rpm) does not exceed 200,000. It is not recommended for heavily loaded steel surfaces unless performance evaluation tests have proven it to be satisfactory. The limitations on speed (DN Value) and on heavily loaded surfaces are related to the properties of the silicone type fluid required by the technical requirements of the specification.

MIL-G-15793 and MIL-G-15719A

Not shown in Table III, these specifications also cover synthetic oil greases. MIL-G-15793, "Grease Instrument," is an ester type product for use over the −65° to +250°F range. It does not possess any outstanding properties not available in MIL-G-3278A or MIL-G-7118A Greases and appears to parallel these products as to application.

MIL-G-15719A

This specification concerns only the lubrication of antifriction bearings of silicone insulated electric motors operating in the 0° to +300°F range. A

silicone fluid is suggested as the lubricating medium, therefore, the grease is not applicable to heavily loaded bearings.

Temperature Range of Lubricating Greases

The relatively wide temperature range covered by each of the several Military Specifications discussed above cannot be met by conventional mineral oil greases. Certain synthetic fluids are less affected by temperature than the mineral oils; they have higher viscosity indices and lower volatility. When used as all or a major portion of the lubricating fluid the resultant greases are capable of operating over a considerably wider temperature range than those products containing straight mineral oils.

Figure 4 provides a comparison of the temperature range of synthetic and mineral oil greases. The indicated ranges are based on specification requirements and on experience with these products. For any specific application the low temperature limit is dependent on the torque available, whereas the high temperature limit depends on the duration of operation required. The effective range for the mineral, ester and silicone type products is about 290°, 375° and 600°F, respectively. A single silicone oil grease (MIL-G-25013C) covers a wider operating range than two ester type products (MIL-G-7421 and MIL-G-25760) which in turn cover a wider range than the three mineral oil products (MIL-G-10924, MIL-G-7711 and MIL-G-3545).

The diester type lubricants are generally considered the most suitable for greases operating at extreme low temperatures, −65° or even −100°F. Certain of the diesters are sufficiently low in volatility to be used at +250°F. Complex esters are more viscous and less volatile than most of the diesters and are suitable for greases operating in the −40° to +350°F range. Some of the polyester type materials are also applicable to this range.

Silicone oil greases are generally considered for extreme high temperature applications, 400° to 600°F. Chlorinated silicones combine both extreme high and extreme low temperature properties. Greases containing this type material as the lubricating fluid can be used at temperatures as high as 600°F for a short period and as low as −100°F.

Applications

The synthetic oil greases, particularly those of the ester type, have found application in a wide variety of equipment involving antifriction, sleeve and pivot bearings, rotational and oscillatory motion. Lubrication of aircraft accessories such as control, actuator and instrument bearings is one of the principal applications for the low temperature type products. They are also used on fractional horsepower motors of servo mechanisms, tape recorders, gyroscopes and other equipment where low-torque, and long life are required. Use in the bearings of larger electric motors is increasing. They are particularly suited for the lubrication of refrigeration equipment and certain selected products are very effective for the lubrication of ultra high speed bearings (DN Value up to 1,000,000). Because of their excellent lubricity and water resistance they are finding increasing use in outdoor applications at ambient temperatures for the lubrication of sleeve and pivot bearings and for gears.

The silicone type greases, because of their limitations as to high loads and high speeds, have a much narrower field of application than the ester type products. The silicone oil greases are used almost exclusively in antifriction bearings operating at very high temperature (450° to 600°F) or a combination of high and low temperature (−100° to +600°F) and under light loads and at DN Values of 200,000 or less.

The lubrication of instrument bearings is one of the most critical applications of the ester type synthetic oil greases (MIL-G-3278A, 7118A or 7421A). These bearings are extremely small as illustrated by Figure 5 which shows a typical instrument bearing in the eye of an ordinary sewing needle. Generally there is no provision for relubrication or for changing lubricants with seasonal variations or with climatic changes. The grease must provide low-torque and long life at operating temperatures in the −65° to +250°F range. It must also remain stable and protect bearing surfaces during storage for periods up to several years at temperatures in the −80° to +160°F range.

The other extreme as regards bearing size and temperature is the lubrication of wheel bearings of

Courtesy of North American Aviation Inc.

Figure 6 — Wheel and roller bearing from an F-100 Super Sabre. Even larger bearings which surround the wheel brake are in use.

Figure 7 — North American F-100 Super Sabre. The arresting or drag parachute (sometimes called a "drogue"), is ejected on landing to assist brakes by decreasing rolling speed.

high speed jet aircraft. Figure 6 shows the relatively large tapered roller bearing and a wheel of the F-100 Super Sabre, Figure 7. Wheel bearings on fighter aircraft of this type may have an outside diameter as great as eighteen inches. The heat generated by the internal disc brakes at landing speeds up to 150 miles per hour is dissipated through the bearings and may subject the grease to temperatures of the order of 500°F for short periods.

Despite their wide range of application, synthetic oil greases must be considered as specialty products. The volume consumed is very small compared with that of the conventional mineral oil products. In 1957 and 1958 synthetic oil greases represented approximately four per cent of the Military's total grease purchases. It seems probable that this percentage would be even lower for the overall grease industry.

SUMMARY

Extension of the high temperature requirements for synthetic lubricants is anticipated in the near future. Temperatures of about 500°F, now relatively infrequent, will probably be common in three to five years. This will necessitate fluids of improved thermal stability.

To achieve this goal either a breakthrough in chemical lubricants will be necessary "or a super refined" mineral oil may re-enter the field. The development of new and improved additives will also undoubtedly be an important factor.

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